

OFFICE OF NAVAL RESEARCH  
END-OF-THE-YEAR REPORT  
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT or CONTRACT: N00014-97-C-0056

PR Number 98PR02105-02

Fluoroelastomer Fouling Release Coating

Dr. Aslam A. Malik

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8/19/98

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**EOY Report - Part I**  
**OFFICE OF NAVAL RESEARCH**  
**PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT**

PR Number: 98PR02105-02

Contract/Grant Number: N00014-97-C-0056

Contract/Grant Title: Fluoroelastomer Fouling Release Coating

Principal Investigator: Dr. Aslam A. Malik

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Phone Number: (916) 355-3215 Fax Number: (916) 355-2044

E-mail Address: aslam.malik@aerojet.com http address:

- a. Number of papers submitted to refereed journals, but not published: 0
- b. + Number of papers published in refereed journals (for each, provide a complete citation): 0
- c. + Number of books or chapters submitted, but not yet published: 0
- d. + Number of books or chapters published (for each, provide a complete citation): 0
- e. + Number of printed technical reports/non-refereed papers (for each, provide a complete citation): 0
- f. Number of patents filed: 1
- g. + Number of patents granted (for each, provide a complete citation): 6
- h. + Number of invited presentations (for each, provide a complete citation): 1
- i. + Number of submitted presentations (for each, provide a complete citation): 0
- j. + Honors/Awards/Prizes for contract/grant employees (list attached): 2  
(This might include Scientific Society Awards/Offices, Selection as Editors, Promotions, Faculty Awards/Offices, etc.)
- k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this PR number: 1  
Graduate Students: 1  
Post-Doctoral Associates: 0  
including the number of,  
Female Graduate Students: 0  
Female Post-Doctoral Associates: 0  
the number of  
Minority\* Graduate Students: 0  
Minority\* Post-Doctoral Associates: 0  
and, the number of  
Asian Graduate Students: 0  
Asian Post-Doctoral Associates: 0
- l. + Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

+ Use the letter and an appropriate title as a heading for your list, e.g.: b. Published Papers in Refereed Journals, or, d. Books and Chapters published. Also submit the citation lists as ASCII files via email or via PC-compatible floppy disks

\* Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

## Supporting Document for the End-of-the-Year Report

### f. Number of Patents Filed

U.S. Patent Application For "Amorphous Polyether Glycols based on Bis-substituted Fluorinated Oxetanes"

### g. Patents Granted

Fluorinated Diamines and Polymers Formed Therefrom.

U.S. 5,637,772 (1997)

Preparation of Mono-substituted Fluorinated Oxetane Prepolymers

U.S. 5,650,483 (1997)

Mono-substituted Fluorinated Oxetane Monomers

U.S. 5,654,450 (1997)

Co-prepolymers Formed from Mono-substituted Fluorinated Oxetane Monomers and Tetrahydrofuran

U.S. 5,668,250 (1997)

A Process for Preparation of Co-prepolymers From Mono-substituted Fluorinated Oxetane Monomers and Tetrahydrofuran

U.S. Patent: 5,668,251 (1997)

Fluorinated Polyurethane Elastomers prepared from Polyether Co-prepolymers formed from Mono-substituted Fluorinated Oxetane Monomers and Tetrahydrofuran.

U.S. 5,703,194 (1997).

### h. Invited Presentations

Malik, A. A. 3M Technology Forum, January 14, 1998, St. Paul, Minnesota.

Malik, A. A.; Carlson, R. P; Featherstone, T. W.; Palandoken, H.; Braden, Stringer, J. A.; T. M.; Archibald, T. G. ONR Antifouling Coatings Review, October 22-24 1997, San Diego

### i. Honors/Awards/Prizes

Dr. Aslam Malik has been promoted to Manager, Process Research Chemistry, 1998

Dr. Aslam Malik and Mr. Roland Carlson are the recipients of Aerojet's Technical Innovation Award for 1998.

Dr. Aslam Malik has been nominated by GenCorp as an inductee to the Hall of Fame of Corporate Inventors, 1998

### i. Other Funding:

Agency: GenCorp Aerojet  
Title: Commercialization of Poly Fox technology  
Amount: \$200,000  
Period of Performance: November 1997-November 1998

Relationship to ONR:

Aerojet's program is a product development/application program with emphasis on cost reduction and development of materials for commercial applications such as low friction, abrasion resistant coatings, stain release coatings for fabrics and carpets, and anti-graffiti coatings

**EOY Report - Part II**  
**ONR END-OF-THE-YEAR REPORT**

- a. **Principal Investigator:** Dr. Aslam A. Malik
- b. **Current Telephone Number:** (916) 355-3215
- c. **Cognizant ONR Scientific Officer:** Dr. Kenneth J. Wynne

d. **Program Objective:**

Our goal is to develop novel fluoroelastomers that exhibit fouling release capabilities and to understand the polymer characteristics that influence the adhesion of biofouling organisms to polymeric substrates. We will develop novel fluoroelastomers that are characterized by low glass transition temperature and the ability to form stable, low surface energy coatings with high abrasion resistance and excellent adhesion to substrates. We will study the physical, surface, mechanical, and thermal properties of these polymeric materials to correlate polymer properties with the ability to reduce adhesion of fouling organisms. Based on the results of marine use tests, we will select most promising coating formulations, conduct additional fouling release use tests, and identify one formulation with the most desirable characteristics for further development.

e. **Significant Results:**

A family of highly fluorinated polyether glycols was prepared and incorporated into a polyurethane matrix to give elastomeric materials with extremely high receding contact angles and low surface energy. Fluorinated oxetane monomers, prepared by the reaction of 3-bromomethyl-3-methyloxetane with a commercial mixture of long chain, perfluoroalkylethanol, were polymerized under ring-opening cationic polymerization conditions to give a polyether glycol. Under standard ring-opening polymerization conditions ( $\text{BF}_3 \cdot \text{THF}/1,4\text{-butanediol}$ ), polyether glycols with  $-\text{O}(\text{CH}_2)_4$  units randomly incorporated into the polymer backbone, are obtained. We have found that these defects, either introduced from the butanediol initiator or from co-polymerization with THF, hinders the orientation of the fluorinated side chain and gives materials with inferior surface properties. We have resolved this problem by employing  $\text{BF}_3 \cdot \text{THP}$  as the catalyst and water as an initiator to give defect-free, fluorinated polyether glycols with good molecular weight control. Our next challenge was to incorporate these highly fluorinated polyether glycols into a polymer matrix. Our initial attempts to incorporate this highly fluorinated polyether soft block into a polyurethane matrix were unsuccessful and tacky, low molecular weight materials were obtained. We have now found that the reactivity of these highly fluorinated polyether glycols can be improved substantially by modifying the structure of the end groups. These modified polyether glycols exhibit high reactivity towards electrophiles and when reacted with isocyanates give tack-free polyurethane elastomers. The surface properties of these fluorinated elastomers are dependent on the length/nature of the fluorinated side chain, degree of polymerization of the soft block, and on the cure chemistry. By controlling these variables, we have successfully prepared polyurethane elastomers that exhibit low surface energy (11 dynes/cm), high receding contact angle with water (112 degrees), and good bonding characteristics. Panels coated with these formulations have been prepared and submitted for fouling release studies.

**f. Future Work**

- Establish the effect of degree of polymerization and side chain length of the soft segment on the surface properties of the elastomer.
- Investigate alternate cure chemistries (e.g self curing silicones) to prepare elastomers with fluorinated oxetane-based soft block.
- Investigate the effect of polymer morphology and surface roughness on surface properties
- Scale-up synthesis of fluorinated polyether glycol and develop coating formulations.
- Coat panels with select formulations and test coatings for marine fouling
- Initiate work on synthesis of high molecular weight polyether polymers based on mono- and di-substituted fluorinated oxetane monomers

**g. Graduate Students/Post Doctoral Candidates**

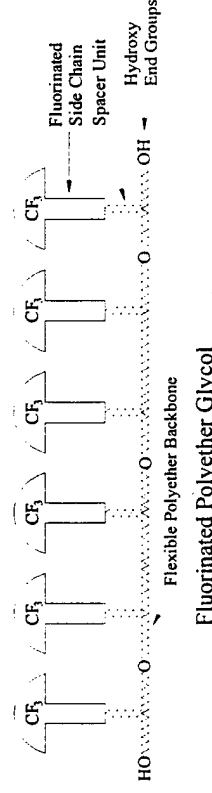
Mr. Jed Hubbs

**Technology Issues:**

Instability of polymer surface towards reorientation highly limits their use in underwater applications, e.g. fouling release coatings

**Objective:**

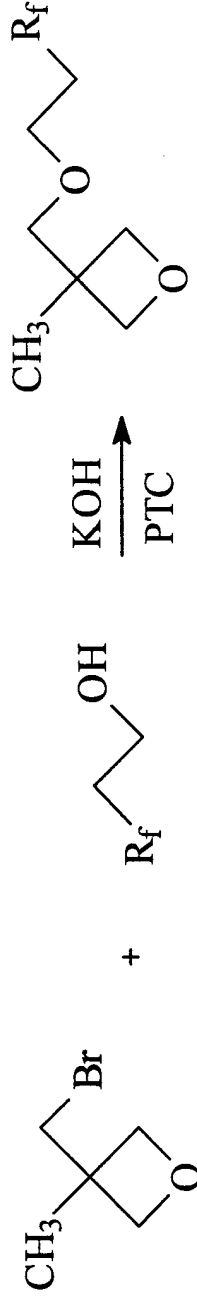
Develop a tough, low surface energy, fluoroelastomer that is stable towards surface reorientation.

**Approach:**

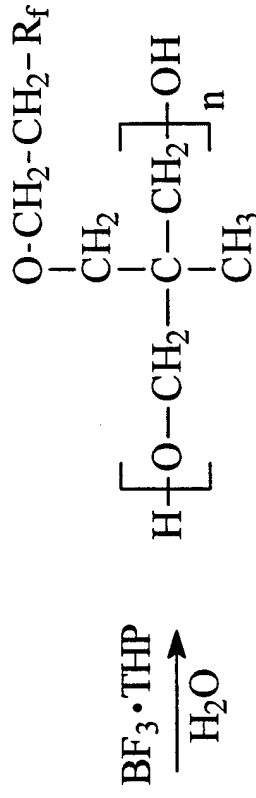
- Prepare defect-free, polyether glycols with linear, highly fluorinated side chains and incorporate these glycols into a polymer matrix.
- New catalyst/initiator system developed for preparing defect-free polyether glycols.
- Novel cure chemistry developed to allow preparation of tough, low surface energy fluoroelastomers.
- Coatings with good adhesion, high  $\theta_{\text{rec}}$  (112 degrees), & high stability towards reorientation were prepared and submitted for marine testing.

**Impact:**

- Discovery of new materials/cure chemistry allows potential to leap-frog silicone fouling release technology
- Validation of new concept
- Economic/environmental benefit



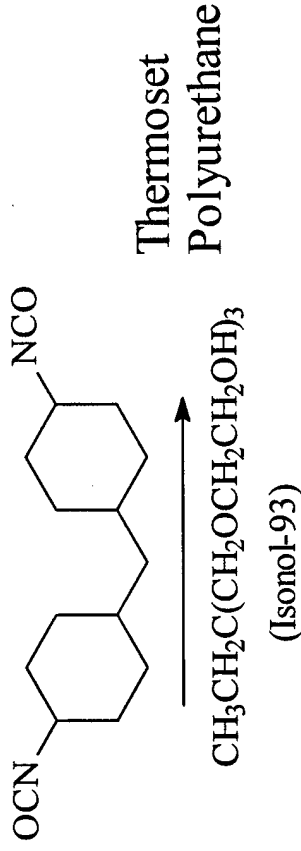
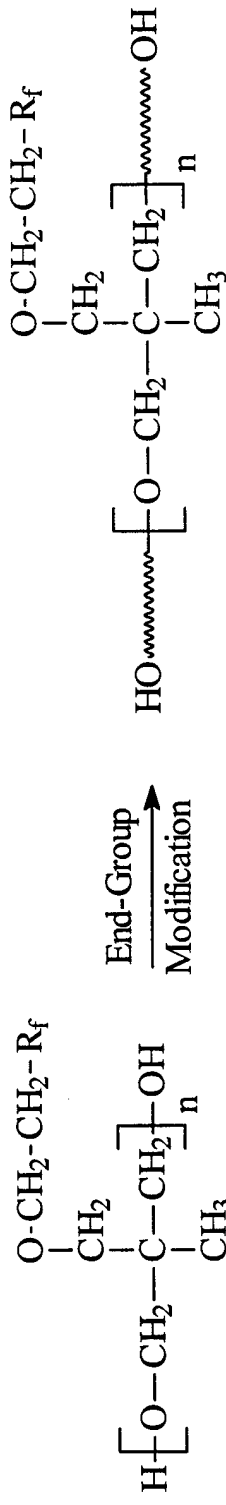
R<sub>f</sub> = Mixture of C<sub>6</sub>F<sub>13</sub>, C<sub>8</sub>F<sub>17</sub>, . . . . C<sub>14</sub>F<sub>29</sub>



Fluorinated Polyether Glycol

- Yield (Overall): 82%
- Nature : Soft Wax
- Degree of Polymerization : 15
- Equivalent wt : 4,342





- Nature: Elastomer
- Surface Energy : 11 dynes/cm
- Critical Surface Tension : 7 dynes/cm
- $\theta_{\text{Adv}}/\theta_{\text{Rec}}$  : 124/112 degrees
- $\theta_{\text{Rec}}$  after 16 h immersion in water : 109 degrees
- Adhesion : Good

## EOY Report - Part III

### d. Explanatory Text

#### Slide #1

Technology Issues: One of the major problems faced with the use of polymeric materials in underwater applications is their instability towards reorientation. For example, a polymer with non-polar groups at polymer/air interface will reorient and expose polar groups when immersed in water to minimize surface free energy. It is postulated that presence of polar groups at polymer/water interface will promote fouling by providing a potential binding site and thus limit the use of these materials in fouling release applications. To be useful as a coating, the polymeric material should be tough and should exhibit good bonding characteristics.

Objective: The main objective of this work is to develop non-toxic, fouling release coatings that are tough and are simple to clean. To prepare such coatings we need to develop materials that are tough elastomers with low glass transition temperatures and will exhibit low surface energy and good adhesion towards substrates. In addition, the candidate polymer should be stable in marine environment and when immersed in water should not exhibit reorientation, that is go from a "low wetting state" (high receding contact angle) to a "high wetting state" (low receding contact angle).

Approach: Prepare and polymerize oxetane monomers that are asymmetrically substituted at the 3-position with a methyl group and a long, linear perfluoroalkyl group. Incorporation of the resulting fluorinated polyether soft block into a polyurethane matrix should yield tough elastomers with surface properties of fluoropolymers and toughness/bonding characteristics of polyurethanes. It is postulated that the perfluoro-alkyl group, attached to the polymer backbone via a flexible spacer group, will microphase separate and migrate to polymer/air interface to give a surface that is dominated by the low surface energy imparting  $-CF_3$  groups. It is further postulated that the mutual attraction between the rigid, linear perfluoroalkyl side chains will provide order in the side chain and thus stabilize the polymer surface towards reorientation.

Accomplishments: Defects, such as those introduced from incorporation of  $-O(CH_2)_4$  units into the fluorinated polyether soft block, disrupt side chain order and thus destabilize the polymer surface towards reorientation. Since the polymerization conditions currently employed do not allow for preparation of defect-free polyether glycols, a new catalyst/initiator system employing  $BF_3 \cdot THP$  as a Lewis acid catalyst and water as an initiator, was developed and successfully used for preparation of defect-free polyether glycols. It should be noted that THP, a stable six-membered cyclic ether, does not copolymerize with fluorinated oxetane monomers and thus is useful in stabilization of  $BF_3$ , as  $BF_3 \cdot THP$  complex.

Incorporation of this highly fluorinated polyether glycol into a polymer matrix presented a yet another challenge. Extension of cure chemistry developed for similar fluorinated glycols, Poly 7-Fox, failed to give tack-free elastomers. Similarly, various attempts to incorporate these highly fluorinated polyether glycol into a thermoset or thermoplastic

polyurethane matrix were unsuccessful. We have now found that by conducting simple end-group modifications it is possible to improve the reactivity of these fluorinated glycols and prepare tough, tack-free elastomers. These elastomers exhibit good bonding characteristics and a surface that is relatively stable towards reorientation as demonstrated by retention of high receding contact angle with water after 16 h immersion in water. Fiber glass panels coated with these formulations have been prepared and submitted for marine testing.

**Impact:** For the first time a tough elastomer that exhibits low surface energy, good adhesion with substrates, and a surface that is relatively stable towards reorientation is available for testing as a fouling release coating. This system will allow us to test some of the basic concepts of fouling release and will allow us to develop the next generation of fouling release coatings. This technology has the potential to leap-frog the existing silicone-based fouling release coating technology and to overcome some of the inherent drawbacks of silicones, such as poor abrasion resistance/tear strength, and adhesion. The economic and environmental benefits to Navy from successful implementation of this technology are enormous.

#### Slide #2

This slide describes the preparation of defect-free, highly fluorinated polyether glycol via a two step process. In the first step, 3-bromomethyl-3-methyloxetane is reacted with long chain perfluoralkyl ethanol under phase transfer conditions to give the corresponding fluorinated oxetane monomer in 85% yield. For this work, a commercial mixture of perfluorinated alkylethanol ( $R_fCH_2CH_2OH$  where  $R_f$  is a mixture of  $-C_6F_{13}$ ,  $-C_8F_{17}$ ,  $-C_{10}F_{21}$ ,  $-C_{12}F_{25}$  and  $-C_{14}F_{29}$ ) was used. In the second step, the fluorinated oxetane monomer is polymerized in the presence of  $BF_3$  THP catalyst and water initiator to give defect-free polyether glycol in near quantitative yield. For this study, a polyether glycol with a degree of polymerization of 15 and a functionality of 2, was prepared and evaluated as a soft segment for elastomers.

#### Slide #3

This slide describes synthesis and characterization of elastomers based on fluorinated polyether glycol soft block. End-group modification of fluorinated polyether glycol followed by the reaction of the modified glycol with isophorone diisocyanate in the presence of a crosslinking agent gave a tough, tack-free polyurethane elastomer. This elastomer exhibited an advancing contact angle of 124 degrees and a receding contact angle of 112 degrees with water. Only a slight decrease in receding contact angle (3 degrees) was observed when the glass slide coated with this material was immersed in water for 16 h. The surface energy of this material (methylene iodide/water method) was 11 dynes/cm, whereas, the critical surface tension (Zisman) was 7 dynes/cm. In addition to good surface properties, these highly fluorinated polyurethane elastomers also exhibited good adhesion to substrates as demonstrated by preparation of fiber glass panels for fouling release coating studies. Panels coated with these materials have been submitted for evaluation as fouling release coatings.